

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including sources, gathering and maintaining the data needed, and completing and reviewing the collection of information aspect of the collection of information, including suggestions for reducing this burden to Washington Headquarters, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Project, Washington, DC 20503.

AFRL-SR-AR-TR-04-

0083

er
ports,
on, DC

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 19 January 2004		3. REPORT TYPE AND DATE COVERED 4/1/99 - 3/31/02 Final Technical Performance Report	
4. TITLE AND SUBTITLE Dynamics of Etching at the Gas-Surface Interface				5. FUNDING NUMBERS Grant No. F49620-99-1-0212	
6. AUTHOR(S) Timothy K. Minton					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Montana State University 207 Montana Hall Bozeman, MT 59717				8. PERFORMING ORGANIZATION REPORT NUMBER 428018/Z0274	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 4015 Wilson Blvd., Rm. 713 Arlington, VA 22203-1954				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approve for Public Release: Distribution Unlimited				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 Words) The essential goals of the project were fulfilled, even though the anticipated breadth of experiments turned out to be overly optimistic. A very detailed experiment on the interactions of hyperthermal O atoms with a hydrocarbon surface has revealed the key initial reactions that occur at the surface, and a new picture of atom-surface scattering has been developed that describes atom-surface collisions in the center-of-mass reference frame, with the incident atom effectively interacting with a finite mass on the surface. Many experiments focused on the interaction of hyperthermal inert (Ar) atoms with continuously oxidized polymer surfaces or continuously chlorinated silicon surfaces. These experiments have shown that collisions of hyperthermal species can enhance etch rates of slowly eroding surfaces by as much as an order of magnitude, suggesting a novel approach to etching fine features into semiconductors and polymers. These experiments involving collision-assisted etching have also shown that the picture of an incident atom colliding with a localized region of the surface may be applied when a hyperthermal incident atom promotes a surface reaction and leads to subsequent ejection of a product from the surface. Thus, many details of etching reactions have been discovered, and a general class of collision-induced etching mechanisms has been described. The novel results of the project have been presented at meetings and in publications, and the new knowledge involving reaction mechanisms related to polymer degradation in low-Earth orbit has been discussed in the space environmental effects community and incorporated into a new ASTM Standard Practice for the testing of materials in an atomic oxygen environment.					
14. SUBJECT TERMS atomic oxygen, hyperthermal neutral beams, gas-surface scattering, etching, collision-induced desorption				15. NUMBER OF PAGES 15	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	
				20. LIMITATION OF ABSTRACT UL	

20040213 108

DYNAMICS OF ETCHING AT THE GAS-SURFACE INTERFACE

Final Technical Performance Report

January 19, 2004

AFOSR-F49620-99-1-0212

Submitted by:

Timothy K. Minton

Department of Chemistry and Biochemistry

108 Gaines Hall

Montana State University

Bozeman, MT 59717

e-mail: tminton@montana.edu

DISTRIBUTION STATEMENT A

Approved for Public Release
Distribution Unlimited

OBJECTIVES

Strategic Objectives

The primary objective of this research project is to elucidate fundamental chemical and physical processes that contribute to the etching of polymers and semiconductors in dry etching environments. This fundamental knowledge should help enable the design of novel etch processes for specialty applications where fine features with high aspect ratios are critical. The new knowledge generated by this project will not only suggest new etch processes, but it will add new understanding to the mechanisms by which materials degrade in the low-Earth orbital environment and, consequently, will (1) enable the definition of more accurate test methods for the prediction of materials durability in low-Earth orbit and (2) help guide the design of new, more durable, spacecraft materials.

Program Abstract

The pursuit of ever smaller dimensions of circuit patterns for ultralarge scale integration has placed unrelenting demands on plasma etching. Etch rate nonuniformities and peculiar etching topographies hinder the production of very fine structures. Trial-and-error development of process recipes for modern etchers has largely overcome these problems for current technologies, but new solutions are required as targeted device dimensions shrink below 200 nm. A basic understanding of the etching interactions that govern etch rate, profile evolution, and surface roughness is essential to develop the predictive capabilities required for efficient optimization of emerging etch tools and for design of a new generation of reactors.

A clearer understanding of etch mechanisms will also guide the development of new spacecraft that can survive in the harsh oxidizing environment of low-Earth orbit. The energetic collisions between an orbiting spacecraft and atomic oxygen in the residual atmosphere promote oxidation and etching of polymer surfaces. Materials testing for space durability is inherently complicated by the presence of a variety of reactive agents in the test environment (e.g., excited-state neutrals, molecular oxygen, ions, and UV light). The validity of a spacecraft materials test may thus be compromised by interactions that are not representative of those in the space environment. Knowledge of the mechanisms by which specific reactive species etch a surface would lead to more valid testing.

A combination of fundamental and engineering studies is thus proposed with the following goals: (1) detailed understanding of the chemical and physical interactions at the gas-surface interface that initiate and propagate etching; (2) identification of new classes of interactions that may be general to many etch chemistries; (3) new etch processes for defining sub-micron features in polymer and semiconductor surfaces; and (4) improved predictions of materials durability in Earth's upper atmosphere.

Molecular beams will be used for controlled studies of gas-surface interactions and for etching materials in well-defined environments. The funds sought here will exploit the capabilities of an existing \$1M molecular beam facility. The apparatus is unique in its coupling of a high-flux, large-area, hyperthermal beam source with a crossed molecular beams apparatus. The source is capable of producing reactive atoms or molecules with velocities in the range $3\text{--}11\text{ km s}^{-1}$. These neutral species will be directed at target surfaces. A rotatable mass spectrometer detector, combined

with modulation techniques, will be used to identify inelastically and reactively scattered products and determine their velocities and directions. The detector is also ideal for source characterization, which will make it possible to tune exposure conditions during optimization of new etch processes.

Collaborators from government, industry, and academia will provide unique materials for these studies, including diamond-like coatings, gallium nitride, and various thermal control materials intended for use in space. These collaborators, who are experts in their respective fields, will also participate in the design and evaluation of the experiments that will explore new etch processes.

SUMMARY OF EFFORT

The essential goals of the project were fulfilled, even though the anticipated breadth of experiments turned out to be overly optimistic. A very detailed experiment on the interactions of hyperthermal O atoms with a hydrocarbon surface has revealed the key initial reactions that occur at the surface, and a new picture of atom-surface scattering has been developed that describes atom-surface collisions in the center-of-mass reference frame, with the incident atom effectively interacting with a finite mass on the surface. Many experiments focused on the interaction of hyperthermal inert (Ar) atoms with continuously oxidized polymer surfaces or continuously chlorinated silicon surfaces. These experiments have shown that collisions of hyperthermal species can enhance etch rates of slowly eroding surfaces by more than an order of magnitude, suggesting a novel approach to etching very fine features into semiconductors and polymers. These experiments involving collision-assisted etching have also shown that the picture of an incident atom colliding with a localized region of the surface may be applied when a hyperthermal incident atom promotes a surface reaction and leads to subsequent ejection of an atom, radical, or molecule from the surface. Thus, many details of etching reactions have been discovered, and a general class of collision-induced etching mechanisms has been described. The novel results of the project have been presented at meetings and in publications, and the new knowledge involving reaction mechanisms related to polymer degradation in low-Earth orbit has been discussed in the space environmental effects community and incorporated into a new ASTM Standard Practice for the testing of materials in an atomic oxygen environment. Therefore, all four goals stated explicitly in the project abstract have been met. In addition, the techniques and infrastructure that have been developed and supported by this project have been applied to the understanding of energy accommodation during aerobraking of spacecraft and in the preparation of surfaces for laser desorption mass spectrometry.

ACCOMPLISHMENTS/NEW FINDINGS

Reactive and inelastic scattering dynamics of hyperthermal oxygen atoms on a saturated hydrocarbon surface. The dynamics of the interactions of hyperthermal atomic oxygen with the surface of a saturated hydrocarbon liquid, squalane, have been investigated. Pulsed beams containing high-velocity ($\sim 6\text{--}8\text{ km s}^{-1}$) O atoms were directed onto a squalane surface, and the volatile products, O, OH, and H₂O, were observed by mass spectrometry as a function of incident angle, final angle, and incident O-atom energy. All product time-of-flight distributions revealed

thermal and non-thermal interaction channels. Direct inelastic scattering, in which only a fraction of the initial translational energy is lost to the surface, is by far the most probable non-reactive interaction. Only a tiny fraction of incident O atoms appear to reach thermal equilibrium with the surface before desorbing. The most likely initial reaction is gas-phase-like H-atom abstraction to form OH, which often leads to scattered OH products with hyperthermal translational energies. An observed hyperthermal H₂O signal can be explained by a sequential direct H-atom abstraction mechanism involving initial formation of OH and subsequent abstraction of another hydrogen atom, with both steps occurring on a time scale too short for thermal equilibrium at the surface to be achieved. Thermal OH and H₂O products are believed to follow thermal accommodation of the initial OH product on the surface. Once the OH becomes accommodated on the surface, it may desorb thermally or abstract a hydrogen atom to form H₂O, which may also desorb thermally. We thus concluded that the first step toward volatile reaction products, whether thermal or hyperthermal, is a direct reaction to produce OH. The initial reactive and non-reactive events have been described in the center-of-mass (c.m.) reference frame with the use of a kinematic picture (Newton diagram) that allows the determination of the effective surface mass encountered by an incident O atom, the c.m. collision energy, and the fraction of the c.m. collision energy that is converted to internal energy in the surface and in the recoiling gaseous species. Center-of-mass product velocity flux maps of OH show predominantly sideways and backward scattering, which would be consistent with a single-collision mechanism that proceeds through a relaxed collinear O-H-C transition state or with a multiple-collision mechanism in which OH that is formed by a stripping mechanism scatters forward and recoils from a nearby head-on collision with a surface moiety.

Collision-assisted erosion of oxidized graphite and hydrocarbon surfaces. The role of energetic collisions in promoting material removal during steady-state erosion of a hydrocarbon polymer under atomic oxygen attack has been investigated by directing hyperthermal beams containing Ar, N₂, and O₂ at continuously-oxidized polymer surfaces and monitoring the dynamical behavior of the CO₂ (and CO) reaction products. Significant production of CO₂ (and CO) from the continuously-oxidized surfaces was correlated with the impact of the hyperthermal, yet relatively inert, species with the surfaces, indicating a collisional process that assists in material removal from the surface. The observation of an analogous collisional process for various hyperthermal species bombarding different oxidized polymer surfaces suggests that the collisional process is generic. The origin of this process could involve an enhancement in the removal rate of CO or CO₂ reaction products already residing on or imbedded in the surface (chemically-enhanced physical sputtering) or collision-induced reactions that lead to formation of volatile CO and CO₂ (chemical sputtering). The dynamical behavior of the CO and CO₂ products in conjunction with a kinematic analysis, suggest a simple picture of the sputtering as an initial binary collision between an incident Ar atom and a localized region of the surface, which is followed by inelastic scattering of the Ar atom and breakup of the local surface moiety into an ejected CO or CO₂ molecule and a local collection of surface atoms that recoil as a group into the surface. The intensity of the CO and CO₂ signals produced from the sputtering process exhibited a strong dependence on Ar-atom-surface collision energy up to 22 eV, with an apparent threshold near 8 eV. The collisional processes that have been studied may be regarded as a synergistic effect in which collisions of energetic particles enhance the erosion rates of hydrocarbons and carbon in atomic oxygen environments. For example, collisional, or sputtering,

processes such as those identified in these experiments may be important in the erosion of materials in the low-Earth orbital environment, as a result of highly energetic collisions of ambient N_2 with oxidized surfaces, and also in ground-based test facilities that subject oxidized surfaces to bombardment by O_2 molecules with very high translational energies.

Collision-induced desorption of Cl from a chlorinated silicon surface. Chlorine chemistry is commonly used to etch silicon. From earlier work, it is known that when molecular chlorine (Cl_2) encounters a fresh Si(100) surface, it dissociatively chemisorbs. The covalent Si-Cl bonds that are formed have an energy of about 4 eV. We have studied the collision-induced desorption (CID) of Cl from a chlorinated silicon surface when an inert atom (Ar) strikes the surface. This study is the first of its kind to probe CID of a covalently bound surface species, and it is made possible with the use of a unique hyperthermal atomic beam source. Beams of Ar atoms possessing kinetic energies in the range 9 - 23 eV were directed at continuously chlorinated surfaces, and the dynamical behavior of scattered Ar and Cl were monitored with a rotatable mass spectrometer detector. The collisional processes proceed via two basic pathways: reactive collisions (desorption of Cl) and inelastic scattering (Ar scatters from the surface and Cl remains on the surface). The flux of desorbed Cl increases dramatically with incident Ar translational energy above ~9 eV, regardless of incident Ar angle, suggesting total energy scaling. Time-of-flight distributions of scattered Ar and Cl exhibit two populations, corresponding to products that exit the surface in a distribution of velocities given by the surface temperature (thermal) and corresponding to products that exit the surface at hyperthermal velocities. In both cases, the hyperthermal populations are overwhelmingly dominant. The average translational energies of scattered hyperthermal Ar and desorbed hyperthermal Cl increase with incident Ar translational energy and with increasing scattering angle (away from the surface normal). The angular distributions of hyperthermally scattered Ar and Cl flux are asymmetric with respect to the surface normal. The flux of Ar peaks at specular angles, while the angle of maximum scattered Cl flux varies little from 60° for Ar incident angles of 45° and 60° . The similar dynamical behavior of inelastically scattered Ar and hyperthermally desorbed Cl indicates that direct impulsive collisions are the dominant pathway to desorbed Cl. The scattering of inelastically scattered Ar and hyperthermally desorbed Cl have been described in terms of a kinematic model in which an incident gas-phase species strikes a localized region of a surface that has an effective mass, and this localized region has the capability to release Cl.

Collision-assisted etching of Si under atomic Cl attack. Hyperthermal Ar-atom bombardment of Si that is continuously chlorinated by Cl_2 may lead to desorption of Cl from the surface, but it does not result in etching of Si. However, when Si is chlorinated by atomic Cl, hyperthermal bombardment by Ar atoms may lead to desorption of Cl and the ejection of a variety of silicon-containing species ($SiCl_x$, $x = 1-4$). An RF discharge was used to create an effusive beam of Cl atoms that continuously bathed a Si(100) surface. Concomitant with the atomic Cl bombardment of the Si surface, a hyperthermal Ar atom beam was directed at the surface, with various incident energies in the range 8 - 23 eV, and products that scattered from the surface were monitored with a rotatable mass spectrometer detector. The data clearly show a collisional process that enhances the production of volatile $SiCl_x$ and thus the etch rate of Si. The intensities of these silicon chlorides decreased with increasing number of chlorine atoms, indicating a process of sequential chlorination. The reaction

processes involved in the etching of Si must consist of three steps: (1) adsorption of Cl on the Si surface; (2) chemical reaction with Si to form an etch product; and (3) product desorption. The enhancement of Si etching by collisions of energetic Ar atoms is due to the acceleration of at least one of the three steps. In the energy range of incident Ar beams used in this experiment, acceleration of step (1) is expected to have no effect because the surface is in a steady-state of continuous chlorination at all times except during the relatively short Ar-atom pulse. Thus, Si etching must be enhanced via acceleration of steps (2) and/or (3). The observation that the average energy of scattered hyperthermal products scales with incident Ar energy and detection angle indicates a direct collision process in which momentum transfer is dominant and some memory of the incident Ar atoms is retained. When an energetic Ar atom hits the surface, it encounters a localized surface moiety, so the interaction involves a cascade of moving target atoms, or in other words, a collision cascade. The result of the collision cascade is the ejection of products that exit in two populations: thermal and hyperthermal (similar to what was seen in the collision-induced desorption of Cl – see above). Two direct reaction mechanisms are possible for the formation of scattered hyperthermal products, chemically-enhanced physical sputtering and chemical sputtering. In chemically-enhanced physical sputtering, the chemical reactions produce more weakly bound products on the surface, thus lowering the binding energy. The sputtering yield is inversely proportional to the binding energy, so the sputtering yield is enhanced. In this mechanism, the main role of the incident Ar atom is to remove products during the energetic collision cascade – i.e., increasing the rate of step (3). When Cl atoms adsorb and react with the Si surface, the binding energies of silicon chloride products (SiCl_x) are lower than that of a Si atom in the lattice. In our experiment, chemically-enhanced physical sputtering is essentially synonymous with collision-induced desorption (CID), which was first used to explain the reaction mechanism of hyperthermal Cl with Si. In the case of chemical sputtering, the energy transfer to the surface from the incident Ar atom may promote a chemical reaction and lead to product formation and desorption. The key difference between chemically-enhanced physical sputtering and chemical sputtering is that for the latter case, the products are formed during the collision cascade. Thus in a chemical sputtering process, the collisions of energetic Ar with the surface increase the rate of both steps (2) and (3).

The products that are ejected from the surface via either sputtering mechanism may desorb during or after the collision cascade. When the products are ejected during the collision cascade, they may leave the surface with hyperthermal energies and thus contribute to the hyperthermal components of the products. The average translational energies of the hyperthermal components are only about 6% of the incident Ar translational energy, which indicates that most of the incident energy is partitioned between kinetic energy in the inelastically scattered Ar atoms and internal energy in the localized surface moiety. Energy in the latter allows the reaction to occur and the products to overcome the binding energy to the surface. The small amount of translational energy in the desorbed hyperthermal products relative to the incident energy is a common phenomenon in ion assisted etching of semiconductors. This kind of energy partitioning is a consequence of significant bond breaking and formation during the collision cascade. The products formed in the collision cascade may collide with another surface region and become trapped on the surface and reach thermal equilibrium and desorb later, which leads to the thermal population of the products. Both thermal and hyperthermal signals are therefore believed to originate from the same sputtering mechanism, which is supported by observations that the fractions of thermal signals remain

unchanged for different incident Ar translational energies. The thermal components in the TOF distributions of scattered products clearly show a measurable surface residence time. However, the surface residence time shown in the TOF distributions is different from the duration that the trapped products stay on the surface before desorption. The surface residence time in the TOF distributions are relative to zero flight time, which is the instant at which Ar atoms with the average translational energy of the beam hit the surface. The apparent surface residence times in the TOF distributions are caused by a decrease of product surface coverage following impingement of Ar atoms on the surface. If the product surface coverage is not directly dependent on the collisions of Ar atoms, the desorbing rate will be constant. However, when the thermal desorption of products is caused by collisions of Ar atoms, the surface coverage will decrease after the collisions, and usually follows first order desorption kinetics. In our experiment, the measured 700 μ s surface residence time (SiCl_3 at T_s of 321 K) combined with the repetition rate of 2 Hz for Ar beam indicates that the product surface coverage went back to the initial level before the next pulse of Ar beam. The surface residence time thus depends on the formation and desorption rates of trapped products, particularly, the surface temperature, incident Ar translational energy, and binding energy.

The surface residence time decreases with increasing surface temperature (figure 6). This observation can be explained as follows. When the surface temperature is increased, the spontaneous etch rate of Si by the atomic chlorine beam alone increases while the Ar beam collisional enhancement becomes relatively less dominant. This can be seen in figure 6, where the intensity of SiCl_3 decreases with increasing surface temperature. The thermal desorption rate of trapped SiCl_3 (without the help from collisions) will also increase with surface temperature, which makes the contribution from collisions of the Ar beam less important. At a certain surface temperature (some value less than 476 K), decrease of product surface coverage caused by collisions of Ar atoms becomes small enough that the surface residence time in the TOF distributions cannot be detected anymore. The surface residence time of SiCl_3 appears to be independent of the incident Ar beam energy in the range of our experiment, which might be too small to cause a measurable difference in surface residence time. In a study of Ar^+ -enhanced Si- Cl_2 reaction, Sawin et al. observed that the surface residence time of SiCl_4 increased with increasing ion energy for a given Cl_2/Ar^+ ratio and increased with decreasing Cl_2/Ar^+ ratio for a given ion energy. They proposed that this observation was the result of a decrease in the amount of chlorine on and in the top layers of silicon. This explanation is consistent with ours because a lower surface concentration of chlorine will lead to greater depletion of products on the surface after the beam of Ar^+ strikes the surface, which results in a longer surface residence time. The surface residence time of different products will be different due to different binding energies. The surface residence time of SiCl_4 at a T_s of 321 K is 65 μ s, which is significantly less than 700 μ s for SiCl_3 . The binding energy of SiCl_4 is significantly less than that of SiCl_3 , thus the contribution from impingement of the Ar beam to the thermal desorption rate of SiCl_4 will be much less important, resulting a lower surface residence time.

The collisional enhancement of Si etching is significant, and the rate of formation of etch products increases dramatically with increasing incident Ar translational energy above a threshold of ~ 8 eV. Similar behavior for different combinations of incident and scattering angles indicates that the total incident energy, rather than the component of the incident energy normal to the surface, governs the collisional enhancement of the product signal. This observation is consistent with the

rough etched surface, which strongly couples parallel energy with normal energy. In order to test the effect of collisional enhancement, we conducted a practical etching experiment in which the etch yield of an Si wafer under exposure to the effusive Cl plasma source with and without the addition of the pulsed hyperthermal Ar beam was compared. The etch yield was determined by placing a screen over the samples during exposure and measuring the etch depth with a profilometer. The samples were exposed for 14 hours. The etch yield when the sample was exposed to both beams was approximately 7 times higher than the etch yield observed when only the effusive Cl beam was used to expose the sample, even though the Ar beam was only pulsed at 2 Hz and had a temporal width of roughly 100 μ s. The collisional process may be regarded as a synergistic effect of the simultaneous bombardment of an eroding/etching surface and an energetic species, and this process appears to be general. Note that similar phenomena were observed in studies of collision-assisted erosion of polymers and graphite.

Energy accommodation in hyperthermal gas-surface collisions. The techniques developed in support of this project were applied to the understanding of energy accommodation of hyperthermal species. This application resulted from request to assist the Mars Global Surveyor Program to understand energy deposition on spacecraft surfaces during aerobraking of spacecraft in planetary atmospheres. The infrastructure that had been developed in the PI's laboratory was ideally suited to the understanding of energy accommodation in the relevant regime of collision energies. Molecular beam-surface scattering experiments were used to measure the fractional energy transfer and relative flux of hyperthermal Ar atoms and CO₂ molecules at a variety of scattering angles when these species scattered inelastically from representative spacecraft materials after impinging at incident angles of either 30 deg or 0 deg with respect to the surface normal. Empirical relationships were derived in order to permit averaging of energy transfer and flux over the entire scattering hemisphere. The overall fractional energy transfers, or translational energy accommodation coefficients, were thus determined. Energy accommodation coefficients were large (>0.9) for both CO₂ and Ar, suggesting that internal degrees of freedom in the CO₂ molecules play a negligible roll in energy transfer for impact velocities of roughly 4.3 km s⁻¹ and 7.5 km s⁻¹ on the selected surfaces. It is likely that energy accommodation coefficients for inelastic scattering will generally be similarly large when atoms or molecules encounter very rough surfaces (such as the model spacecraft surfaces used in these experiments) that allow for multiple collisions which tend to drive the gaseous species into thermal equilibrium with the surface. These large energy accommodation coefficients suggest that hyperthermal gas-surface collisions during aerobraking convert translational energy very efficiently into heat at spacecraft surfaces.

Laser-induced desorption-ionization of organic compounds from etched silicon and carbon surfaces. The hyperthermal beam source that formed the basis for this project was used in a spin-off application to prepare roughened surfaces for the study of laser-desorption ionization mass spectrometry. The results showed promise for the use of hyperthermal beams to prepare such surfaces, and a proposal for follow-on work may be forthcoming. The laser-induced desorption/ionization of organic compounds from etched carbon and silicon substrate surfaces was investigated, and the results were compared for surfaces that were etched by two different methods. Silicon surfaces were etched either by galvanostatic anodization to produce porous silicon or by a

hyperthermal (~5 eV) F-atom beam to produce nonporous silicon. Atomic force microscopy images showed that both etching procedures yielded surfaces with submicron structures. Highly oriented pyrolytic graphite was etched with a beam of hyperthermal O atoms. A 337 nm ultraviolet (UV) laser and a 3.28 μm infrared (IR) laser were used for desorption. Analytes were deposited on the substrates either from the liquid or the gas phase. Mass spectra were obtained provided that three conditions were fulfilled. First, sufficient laser light had to be absorbed. When the IR laser was employed, a thin physisorbed solvent layer was required for sufficient laser light absorption to occur. Though the required fluence of IR and UV light differed by a factor of about 20, the calculated maximum surface temperatures were similar, about 1000K. The second requirement was that the substrate had a rough surface. The third requirement, for the observation of protonated analytes, was that the aqueous pK_a -value of the analyte be larger than about 4. These observations support the conclusion that the desorption-ionization mechanism of analytes from porous and nonporous surfaces are very similar or essentially the same. The gas-phase-introduced analytes must have been adsorbed as neutrals on the surface and then protonated in a solvating environment. The ion desorption process is induced by laser heating, and localized electric fields can serve both to promote ion desorption and charge separation in the surface.

PERSONNEL SUPPORTED

Year 1 (4/1/99 - 3/31/00)

- a) Timothy K. Minton, Montana State University PI (25%)
- b) Donna Garton, staff member (100%)
- c) Jianming Zhang, graduate student (100%)
- d) Chiang-Lin Fong, graduate student (25%)
- e) Alexis Foreman, part-time undergraduate student (100%)

Year 2 (4/1/00 - 3/31/01)

- a) Timothy K. Minton, Montana State University PI (25%)
- b) Donna Garton, staff member, 4/1/00 - 8/15/00 (100%)
- c) Donna Garton, graduate student, 8/16/00 - 3/31/01 (14%)
- c) Jianming Zhang, graduate student (100%)
- d) Chiang-Lin Fong, graduate student (67%)
- e) Alexis Foreman, part-time undergraduate student, 4/1/00 - 12/31/00 (100%)

Year 3 (4/1/01 - 3/31/02)

- a) Timothy K. Minton, Montana State University PI (10%)
- b) Donna Garton, graduate student (5%)
- c) Jianming Zhang, graduate student, 4/1/01 - 8/30/01 (100%)

PUBLICATIONS

Student Thesis

1. "Studies of Gas-Surface Interaction Dynamics with Hyperthermal Neutral Beams," Jianming Zhang, Ph.D. Thesis, August 2001.

Book Chapter

2. "Dynamics of Atomic-Oxygen-Induced Polymer Degradation in Low Earth Orbit," T. K. Minton and D. J. Garton, in *Chemical Dynamics in Extreme Environments: Advanced Series in Physical Chemistry*, R. A. Dressler, ed. (World Scientific, Singapore, 2001) pp. 420-489.

Journal Articles

3. "Collision-Assisted Etching of Si in an Atomic Chlorine Environment," J. Zhang and T. K. Minton, to be submitted to *J. Vac. Sci. Technol. A* (2004). (draft completed)
4. "Collision-Induced Desorption of Chlorine from a Chlorinated Silicon Surface," J. Zhang and T. K. Minton, to be submitted to *J. Chem. Phys.* (2004). (draft completed)
5. "Energy Accommodation in Hyperthermal Gas-Surface Collisions: Relevance to Aerobraking in Planetary Atmospheres," T. K. Minton, M. Tagawa, and G. M. Nathanson, *J. Spacecraft and Rockets*, in press (2004).
6. "Reactive and Inelastic Scattering Dynamics of Hyperthermal Oxygen Atoms on a Saturated Hydrocarbon Surface," J. Zhang, D. J. Garton, and T. K. Minton, *J. Chem. Phys.* **117**, 6239-6251 (2002).
7. "Production of Volatile CO and CO₂ from Oxidized Polyethylene and Graphite Surfaces by Hyperthermal Atom-Surface Collisions," J. Zhang and T. K. Minton, *High Perform. Polym.* **13**, S467-S481 (2001).
8. "On the Mechanism of Laser-Induced Desorption/Ionization of Organic Compounds from Etched Silicon and Carbon Surfaces," S. Alimpiev, S. Nikiforov, V. Karavanskii, T. K. Minton, and J. Sunner, *J. Chem. Phys.* **115**, (2001).

Conference Proceedings

9. "Hyperthermal Reactions of Oxygen Atoms with Saturated Hydrocarbons," T. K. Minton, D. J. Garton, and H. Kinoshita, in *Proceedings of the 6th International Conference on Protection of Materials and Structures from the Space Environment*, Toronto, Canada, May 1-3, 2002.
10. "Atomic-Oxygen-Assisted Materials Degradation in LEO: Collision-Enhanced Erosion, Another Synergistic Effect," J. Zhang, D. J. Garton, and T. K. Minton, in *Proceedings of the 8th International Symposium on Materials in a Space Environment and 5th International Conference*

on Protection of Materials and Structures from the LEO Space Environment, Arcachon, France, June 5-9, 2000.

11. "Energy Accommodation in Gas-Surface Collisions: Relevance to Mars Aerobraking," T. K. Minton, M. Tagawa, and G. M. Nathanson, in *Proceedings of the 8th International Symposium on Materials in a Space Environment and 5th International Conference on Protection of Materials and Structures from the LEO Space Environment*, Arcachon, France, June 5-9, 2000.

12. "Materials Degradation in Low Earth Orbit: An Oxygen Atom's Accomplice," T. K. Minton, D. J. Garton, J. Zhang, and J. W. Seale, in *Proceedings of the 6th Japan International SAMPE Symposium & Exhibition (JISSE-6)*, Tokyo Big Sight, Tokyo, Japan, October 26-29, 1999.

INTERACTIONS/TRANSITIONS

Participation/presentations at meetings, conferences, seminars, etc.

1. "Reactive and Inelastic Scattering Dynamics of Fast Oxygen Atoms with Hydrocarbon Surfaces," 1999 *Gordon Research Conference on Dynamics at Surfaces*, Andover, NH, August 8-13, 1999. (invited talk)

2. "Dynamics of Polymer Etching at the Gas-Surface Interface," 218th *American Chemical Society National Meeting*, New Orleans, LA, August 22-26, 1999. (invited talk)

3. "Interactions of Atomic Oxygen with Hydrocarbon Surfaces: Initial and Steady-State Etching Reactions," Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, January 13, 2000. (invited talk)

4. "Interactions of Atomic Oxygen with Hydrocarbon Surfaces: Initial and Steady-State Etching Reactions," Department of Chemistry, North Carolina State University, Raleigh, NC, February 3, 2000. (invited talk)

5. "Interactions of Atomic Oxygen with Hydrocarbon Surfaces: Initial and Steady-State Etching Reactions," Department of Biological, Chemical, and Physical Sciences, Illinois Institute of Technology, Chicago, IL, February 10, 2000. (invited talk)

6. "Dynamics of Atomic-Oxygen-Induced Erosion of Polymers in Low Earth Orbit," 220th *American Chemical Society National Meeting*, Washington, DC, August 20-24, 2000. (invited talk)

7. "Gas-Surface Scattering Dynamics in Low Earth Orbit: Polymers under Atomic Oxygen Attack," Department of Chemistry, University of Illinois, Urbana, IL, September 20, 2000. (invited talk)

8. "Gas-Surface Scattering Dynamics in Low Earth Orbit: Polymers under Atomic Oxygen Attack," Department of Chemistry and Biochemistry, The University of Notre Dame, Notre Dame, IN, September 21, 2000. (invited talk)

9. "Gas-Surface Scattering Dynamics in Low Earth Orbit: Polymers under Atomic Oxygen Attack," Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA, October 30, 2000. (invited talk)
10. "Gas-Surface Scattering Dynamics in Low Earth Orbit: Polymers under Atomic Oxygen Attack," Air Force Research Laboratory, Edwards AFB, CA, November 1, 2000. (invited talk)
11. "Gas-Surface Scattering Dynamics in Low Earth Orbit: Polymers under Atomic Oxygen Attack," University of Wisconsin, Milwaukee, February 9, 2001. (invited talk)
12. "Gas-Surface Scattering Dynamics in Low Earth Orbit: Polymers under Atomic Oxygen Attack," Tufts University, Medford, MA, February 21, 2001. (invited talk)
13. "Gas-Surface Scattering Dynamics in Low Earth Orbit: Polymers under Atomic Oxygen Attack," University of Illinois, Chicago, March 2, 2001. (invited talk)
14. "Collision-Induced Chemical Processes on a Chlorinated Surface," 221st American Chemical Society National Meeting, San Diego, CA, April 1-5, 2001. (invited talk)
15. "Gas-Surface Scattering Dynamics in Low Earth Orbit: Polymers under Atomic Oxygen Attack," University of Utah, Salt Lake City, April 9, 2001. (invited talk)
16. "Gas-Surface Scattering Dynamics in Low Earth Orbit: Polymers under Atomic Oxygen Attack," University of Colorado, Boulder, April 20, 2001. (invited talk)
17. "Collision-Induced Chemical Processes on a Chlorinated Silicon Surface," *AFOSR Molecular Dynamics Contractor's Meeting*, Newport Beach, CA, May 21-23, 2001. (invited talk)
18. "Reactive Scattering Dynamics of Fast Oxygen Atoms with Hydrocarbon Surfaces: Initial and Steady-State Reactions," T. K. Minton, D. J. Garton, J. Zhang, and J. W. Seale, 46th *International Symposium of the American Vacuum Society*, Seattle, WA, October 25-29, 1999. (contributed talk)
19. "Atomic-Oxygen-Assisted Materials Degradation in LEO: Collision-Enhanced Erosion, Another Synergistic Effect," J. Zhang, D. J. Garton, and T. K. Minton, 8th *International Symposium on Materials in a Space Environment and 5th International Conference on Protection of Materials and Structures from the LEO Space Environment*, Arcachon, France, June 5-9, 2000. (contributed talk)
20. "Inelastic and Reactive Scattering Dynamics of Hyperthermal Oxygen Atoms on a Liquid Hydrocarbon Surface," J. Zhang, D. J. Garton, J. W. Seale, A. K. Frandsen, and T. K. Minton, *XVIIth Conference on the Dynamics of Molecular Collisions*, Lake Harmony, PA, July 18-23, 1999. (poster presented by student)

21. "Energy Accommodation in Gas-Surface Collisions: Relevance to Mars Aerobraking," T. K. Minton, M. Tagawa, and G. M. Nathanson, in *Proceedings of the 8th International Symposium on Materials in a Space Environment and 5th International Conference on Protection of Materials and Structures from the LEO Space Environment*, Arcachon, France, June 5-9, 2000. (poster presentation)

22. "Atomic-Oxygen Interactions with Saturated Hydrocarbon Surfaces: Probing Polymer Degradation Mechanisms," D. J. Garton, J. Zhang, and T. K. Minton, in *Proceedings of the 8th International Symposium on Materials in a Space Environment and 5th International Conference on Protection of Materials and Structures from the LEO Space Environment*, Arcachon, France, June 5-9, 2000. (poster presented by student)

Consultative and advisory functions

Prof. Masahito Tagawa, Kobe University, Japan. Prof. Tagawa is the key person in Japan who is studying space environmental effects. He and the PI have collaborated closely on a study of gas-surface energy transfer when energetic CO₂ molecules and Ar atoms strike various surfaces. Energy transfer of fast species with surfaces is very important to drag on spacecraft in planetary orbits and for etching of materials in certain environments. The collaboration with Prof. Tagawa led to a post-doc (Hiroshi Kinoshita) from his lab coming to work in the PI's lab for 1 and 1/2 years. Dr. Kinoshita worked on projects related to the AFOSR grant, although all his funding came from a Japanese scholarship.

Prof. Gilbert Nathanson, University of Wisconsin. Prof. Nathanson collaborated with the PI (and Prof. Tagawa, see above) on a study of gas-surface energy transfer when energetic CO₂ molecules and Ar atoms strike various surfaces.

Chemat Technology, Northridge, CA. The work of the PI on atomic oxygen interactions with polymer surfaces attracted Chemat Technology to collaborate with the PI. Chemat received a NASA SBIR for the development of atomic-oxygen-resistant coatings. These coatings involved the incorporation of silica nanoparticles into silicones. Chemat provided token funding for the PI to test these coatings in his lab. One of the coatings performed exceptionally well, as it showed no erosion upon atomic-oxygen exposure and did not crack or discolor. The results were published as a proceedings paper: "Organic-Inorganic Nano-Hybrid Composite as Atomic Oxygen Durable Coating," Y. Huang, J. Liu, I. Ball, and T. K. Minton, in *Proceedings of the 47th International SAMPE Symposium & Exhibition*, Long Beach, CA, May 12-16, 2002.

ASTM. During the period 1999 - 2000, the PI participated on a committee for the preparation of an ASTM Standard Practice for the testing of materials in an atomic oxygen environment. This Standard Practice is now in widespread use.

Prof. Jan Sunner, Montana State University. The PI used unique hyperthermal beams of atomic oxygen and atomic fluorine to prepare roughened surfaces of highly ordered pyrolytic graphite (HOPG) and silicon, respectively. Prof. Sunner used these surfaces to show that simple surface roughness could enhance the production of ions during laser desorption of adsorbates on surfaces.

MURI Center for Materials Chemistry in the Space Environment. The work supported by AFOSR on this grant served as a springboard for the formation of a group of researchers who have considerably extended the body of scientific research on space environmental effects on materials in low-Earth orbit. This group currently operates an AFOSR-funded MURI center. The PI is an integral part of this group that includes:

Prof. Steven Sibener, University of Chicago
Prof. Luping Yu, University of Chicago
Prof. Dennis Jacobs, Notre Dame University
Prof. George Schatz, Northwestern University
Prof. John Tully, Yale University
Prof. Barbara Garrison, Penn State University
Prof. Bill Hase, Wayne State University

Educational outreach. During a period of summer support on this grant (summer 1999), the PI was an instructor for a week-long workshop on chemistry called "Peaks and Potentials," a summer camp at Montana State University for 6th through 8th grade children.

Transitions

NONE

NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

- Hyperthermal collisions of inert species can accelerate the erosion rate of polymers that are under atomic-oxygen attack. For example, in low-Earth orbit, N₂ molecules may strike oxidized surfaces with collision energies greater than 8 eV and can promote the production of CO and CO₂ from the surface. Depending on a spacecraft altitude (i.e., the relative concentration of N₂), such collisions may increase the erosion rate by as much as an order of magnitude over the erosion rate caused by atomic oxygen alone. Collision-enhanced erosion has thus been identified as another "synergistic effect" in the degradation of materials in the low-Earth orbital environment. In atomic-oxygen test facilities, where sample surfaces are exposed to O₂ molecules with approximately 10 eV of translational energy, the O₂ may be accelerating the erosion of test specimens through the collisional effect that has been identified. The O₂ in certain test environments may thus be inadvertently playing the role of N₂ in the low-Earth orbital environment.

- Collision-induced desorption of Cl from a chlorinated silicon surface and collision-assisted etching of silicon in an atomic chlorine environment have been described in terms of a kinematic model in which an incident gas-phase species strikes a localized region of a surface that has an effective mass, and this localized region has the capability to release Cl or SiCl_x. This kinematic picture allows the identification of the effective mass and helps reveal the dynamics of the gas-surface interaction.

- The work on collision-induced etching (or erosion) suggests that inert atoms may be used to etch fine structures into surfaces that are bathed with a reactive gas. Under conditions where the reactive gas etches the surface very slowly, a beam of energetic atoms (e.g., Ar) could be used to promote the

reaction and thus the removal of material. The energy dependence of the collision-induced etching process is very strong, so atoms that scatter from the surface will not have enough energy to promote collision-assisted etching after the first impact. Inasmuch as multiple collisions can lead to undercutting of etched features, the use of inert atoms to etch surfaces would alleviate the undercutting and allow for extremely anisotropic etching of very tiny features.

- Initial interactions of hyperthermal atomic oxygen with hydrocarbon surfaces have been described as gas-phase-like collisions between incident O atoms and a localized region of the surface with an effective mass near 40 amu. A novel way of viewing gas-surface collisions in the center-of-mass frame has been described, and center-of-mass velocity flux maps have been obtained. We have modified a well-known hard-sphere scattering model to include internal energy transfer in the center-of-mass frame, and this modified model allows the determination of the average fraction of the center-of-mass collision energy that is transferred to the surface.

HONORS/AWARDS

a) award received one month after end of grant, based largely on research conducted during grant period

Charles and Nora L. Wiley Faculty Award for Meritorious Research, May 2002

b) lifetime achievement honors

Aurora Illinois Foundation Undergraduate Scholarship, 1976-80

University of Illinois Summer Fellowship, 1979

NASA Award for a Technological Contribution, 1995

MSU Alumni/Bozeman Chamber of Commerce Excellence Award, 1996

Charles and Nora L. Wiley Faculty Award for Meritorious Research, May 2002

Air Force Research Laboratory, In-House Project of the Quarter: "Space-Survivable Polymers Containing Polyhedral Oligomeric Silsesquioxanes (POSS)", Fall 2002